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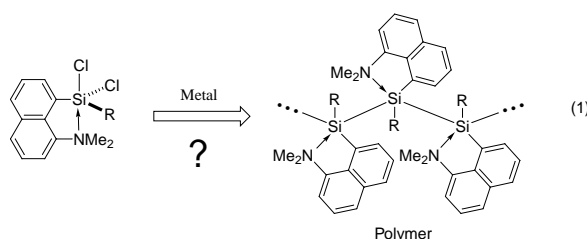
Reaction of Hypercoordinate Dichlorosilanes Bearing 8-(Dimethylamino)-1-naphthyl Group(s) with Magnesium: Formation of the 1,2-Disilaacenaphthene Skeleton

Kohei Tamao, Masahiro Asahara, Tomoyuki Saeki and Akio Toshimitsu

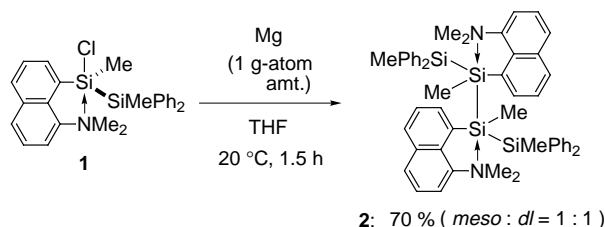
The reaction of a hypercoordinate dichlorosilane bearing an 8-(dimethylamino)-1-naphthyl group(s) with magnesium affords a dimeric product that contains a 1,2-disilaacenaphthene skeleton arising from silicon-silicon and silicon-naphthyl carbon bond formation and amino group migration from the naphthyl carbon atom to the coordinated silicon atom.

keywords: 1,2-disilaacenaphthene / hypervalent compounds / magnesium / silicon / rearrangements

We have clarified that a pentacoordinate monochlorosilane **1** containing the 8-dimethylamino-1-naphthyl group undergoes reductive coupling with magnesium to afford **2**, which provides a new procedure for the direct interconnection of pentacoordinate silicon atoms (Scheme 1).[1] We anticipated that a similar magnesium reduction of a pentacoordinate dichlorosilane containing the same aminonaphthyl group would give polysilanes in which all the silicon atoms are pentacoordinate [eq. (1)]. However, contrary to our expectation, the reaction actually afforded



Scheme 1.



no polysilanes but only a dimeric product that contained a 1,2-disilaacenaphthene skeleton arising from Si—Si and Si—C bond formation and amino group migration from the naphthyl carbon atom to silicon atom (Scheme 2).[2]

The pentacoordinate dichlorosilane **3** bearing an 8-(dimethylamino)-1-naphthyl group was treated with 2 g-atom amounts of magnesium. After quenching with isopropyl alcohol, the dimerized product 1-isopropoxy-1,2-disilaacenaphthene (**4**) bearing only one 8-(dimethylamino)-1-naphthyl group, was obtained as a mixture of

SYNTHETIC ORGANIC CHEMISTRY — Synthetic Design —

Scope of research

(1) Synthesis, structural studies, and synthetic applications of organosilicon compounds, such as pentacoordinate silicon compounds, functionalized silyl anions, and functionalized oligosilanes. (2) Design and synthesis of novel π -conjugated polymers containing silacyclopentadiene (silole) rings, based on new cyclization reactions and carbon-carbon bond formations mediated by the main group and transition metals. (3) Chiral transformations and asymmetric synthesis via organosulfur and selenium compounds, especially via chiral episulfonium and episelenonium ions.



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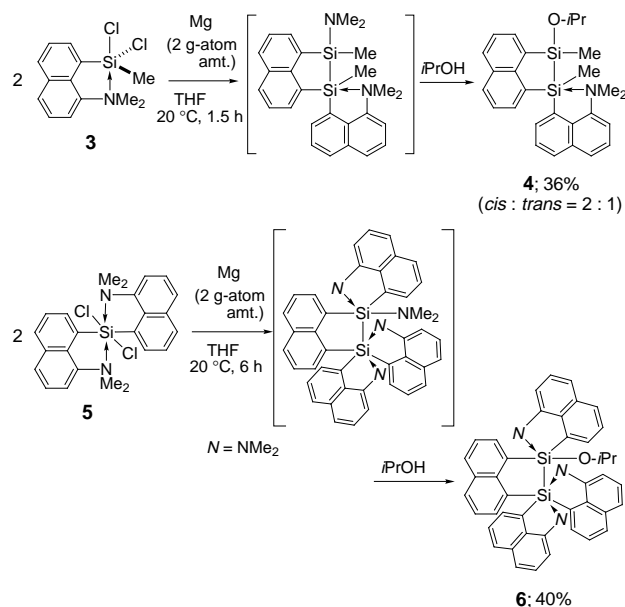


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stereoisomers (*cis:trans* = 2:1). The structure of this quite unexpected product was confirmed by X-ray crystallography on *cis*-**4** (Figure 1) and by ^1H , ^{13}C , and ^{29}Si -NMR spectra of *cis*- and *trans*-**4**. It is noteworthy that the coordination number of one of the two silicon atoms is lowered from five to four.

Scheme 2.



Hexacoordinate dichlorosilane **5** bearing two 8-(dimethylamino)-1-naphthyl groups also reacted with magnesium to afford, after treatment with isopropyl alcohol, 1-isopropoxy-1,2-disilaacenaphthene (**6**), which bears three 8-(dimethylamino)-1-naphthyl groups as the major product (Scheme 2). The structure of this crowded molecule was also determined by X-ray crystallography (Figure 2). One silicon atom is again pentacoordinate while the other is hexacoordinate. Compound **6** is the first disilane composed of hexacoordinate and pentacoordinate silicon centers.

Interestingly, in these reactions, one silicon atom became bonded to the naphthyl carbon atom that bore the amino group. The amino group migrated to the coordinated

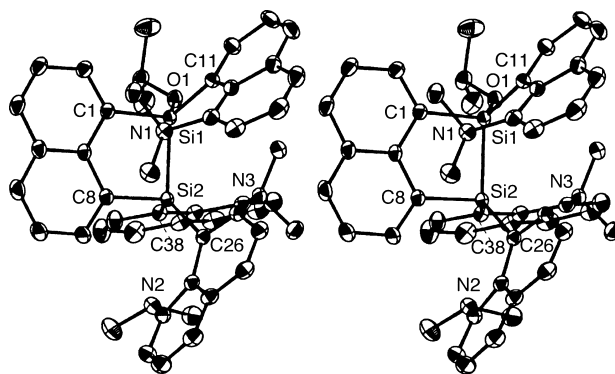


Figure 2. X-ray structure of **6** drawn in stereoview at 30% probability level. All hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (deg): Si1—Si2, 2.3641(6); Si1···N1, 3.078(2); Si2···N2, 3.147(2); Si2···N3, 2.970(2); O1—Si1···N1, 168.06(6); Si2—Si1—O1, 107.17(5); Si2—Si1—C1, 94.35(6); Si2—Si1—C11, 127.54(6); Si1—Si2···N2, 171.97(4); N3···Si2—C8, 175.84(7); Si1—Si2—C8, 89.14(6); Si1—Si2—C26, 122.15(6); Si1—Si2—C38, 104.17(6).

silicon atom to afford an aminosilane with a lower coordination number and was finally substituted by the isopropoxy group during workup with isopropyl alcohol.

Two types of reactions of hypercoordinate dihalosilanes with alkali or alkali earth metals have been reported. One is the conventional silicon—silicon bond formation observed by Beltzner et al. in the reaction of a hypercoordinate dichlorosilane bearing 2-[(dimethylamino)methyl]phenyl group(s) with magnesium to afford the corresponding cyclic trisilane.[3] The other is cyclization by silicon—benzyl carbon bond formation and migration of the amino group from the benzyl carbon atom to the silicon atom without silicon—silicon bond formation. Thus, Corriu, Auner et al. reported the reaction of a pentacoordinate difluorosilane bearing the 8-[(dimethylamino)methyl]-1-naphthyl group with lithium or lithium naphthalenide to afford a 1-silaacenaphthene derivative.[4] In our case, both silicon—silicon bond formation and amino-group migration proceeded concomitantly and selectively in the reaction of **3** and **5** with magnesium to afford the 1-amino-1,2-disilaacenaphthene derivatives. These results indicate that the course of reaction depends on the structure of the aminoaryl groups and suggest the possibility of developing new types of reactions by the introduction of new intramolecular coordinating groups.

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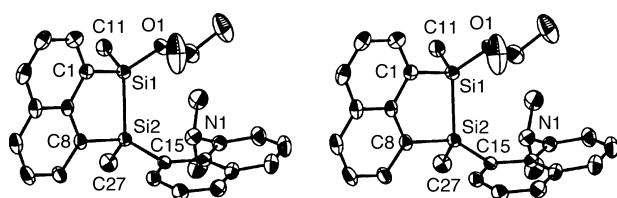


Figure 1. X-ray structure of *cis*-**4** drawn in stereoview at 30% probability level. All hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (deg): Si1—Si2, 2.3469(8); Si2···N1, 2.828(2); N1···Si2—C8, 177.16(8); Si1—Si2—C8, 89.43(8); Si1—Si2—C15, 113.56(7); Si1—Si2—C27, 119.14(9); Si2—Si1—O1, 122.01(7); Si2—Si1—C1, 93.75(7); Si2—Si1—C11, 114.07(9).